Atomistic Investigations into the Dependence of Detonation Properties on Material Parameters using Molecular Dynamics

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In order to experimentally test the dependence of detonation characteristics, e.g., shock velocity (u_s, on a high explosive's (HE's) material properties, e.g., its exothermicity (Q), one is forced to simultaneously vary multiple parameters upon which the detonation may depend. Computational simulations can be used to reduce this complexity and allow the more direct assessment of significant changes in materials properties and how they affect the detonation response.

Molecular dynamics (MD) have been used to simulate detonations. With it one can either attempt to reproduce a known material, or to generate a model material whose parameters can be set arbitrarily. To simulate the detonation process one needs only a representative interaction potential. Here, we use the model potential of Brenner et al. [1] (REBO) that has been the basis of several studies. It is a many-body potential that simulates covalent bonds in an empirical way, thus enabling rapid computation. It describes a simple exothermic reaction: $2AB \rightarrow A_2 + B_2 + 2Q$. The actual code used to model detonation is SPaSM, short for Scalable Parallel Short-range MD, and developed at Los Alamos National Laboratory.

In the systematic process of probing the characteristics of detonation on an HE's material parameters, we follow the work of Haskins and Cook [2], in which they varied Q for their model (based on the simple dissociative reaction $A2 \rightarrow 2A$) from 1 eV to 10 eV. Similar to their results, we found a linear and increasing relationship between Q and u_s^2. Intuitively, this makes sense. The kinetic energy of the detonation shock front, which is related to the square of u_s, should increase with the energy used to drive it, Q. This simple argument suggests that the slope of the linear correlation should be 1, while a value of 0.6 is actually observed. So other factors must be playing a significant role here.

A more complete model for detonation shows that the velocity of an unsupported detonation front can be determined by the initial state of the HE in front of the detonation front and the Chapman-Jouget (CJ) state behind it [3]. The CJ state can be determined by drawing a straight line through the initial state and tangent to the Hugoniot curve (H) on a pressure-volume (PV) state diagram. This line is called a Rayleigh line (R). It is an expression of the conservation of mass and momentum across the detonation front. Its slope is $-(\rho_0 u_s)^2$, where ρ_0 is the initial density of the HE. H is an expression of the conservation of energy across the detonation front. The point where H and R are tangent is the CJ state [3].

In order to quantify the relationship between u_s and Q, we mapped out H for several values of Q. To do this we run a set of microcanonical ensembles (NVE) at a given specific volume (v) until we find the value of the specific internal energy (E) that satisfies H. Then we repeat for different values of v until we can determine the CJ state from the tangency condition. The rather surprising results for the Hugoniots are shown in Fig. 1. We had expected to observe simple non-ideal gas behavior, which would result in smooth hyperbolic-type curves on this plot. Instead, the Hugoniot curves have extensive regions that are near linear, which is rather unusual behavior. The curve for $Q = 1.5$ eV is more complex yet with a downward concave region, which suggests the presence of a phase transition. Despite this unusual behavior, the CJ states determined by the tangency condition show a smooth linear increase with Q. The numbers for u_s from the dynamic simulations of detonation are within 4% of those found by the NVE simulations with the less accurate simulations being of lower

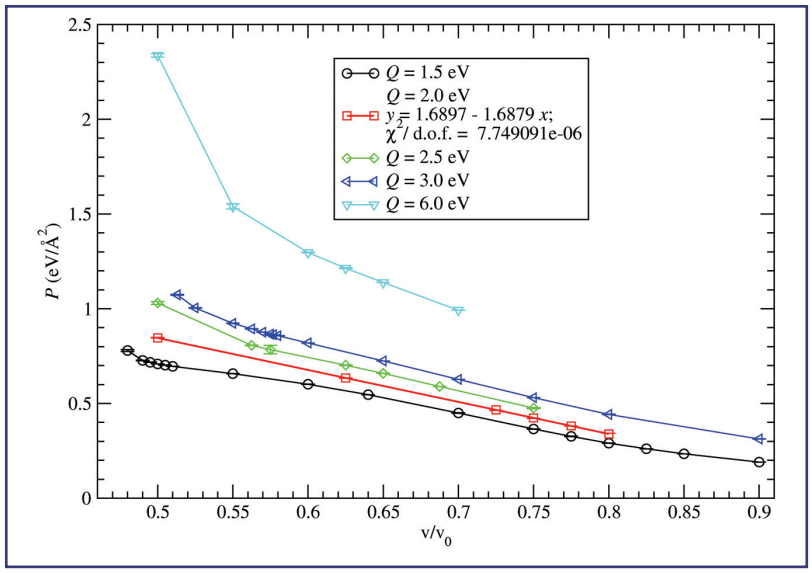

Figure 1—
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Q and closer to failure. This further verifies that these systems are behaving as ideal CJ detonations, and that the u_s dependence on Q is explained by changes in the product equation of state.

The origin of these unexpected changes was determined by a more careful study of the atomistic geometry at the CJ conditions. A snapshot of an NVE at CJ for Q = 3.0 eV is shown in Fig. 2. In it, trimer formation is evident. Such formation has been confirmed by radial distribution calculations in an NVE simulation and potential surface contours of the interaction potential as a function of the distances between three inline particles, A-B-A. The potential surfaces indicate a minimum for trimer formation. Higher oligomers are apparent for the systems with lower values of Q. This dimer-oligomer transition then explains the "phase transition" behavior observed in the Hugoniot curves.

It had not been originally intended that such complex chemistry would result from a seemingly simple potential. Given its presence, the rather simple Q vs u_s dependence is a rather surprising result and raises a cautionary flag in interpreting "obvious" results too quickly. Modifications to this potential have now been developed that eliminate this trimer/oligomer formation [4] and comparative studies are underway.

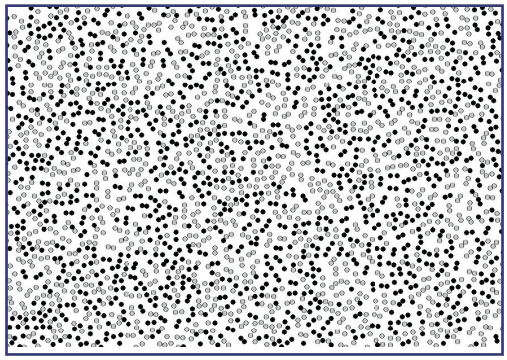

Figure 2—
Snapshot of NVE at CJ. A atoms are black and B gray.

[1] D.W. Brenner, et al., "Detonations at Nanometer Resolution using Molecular Dynamics," *Phys. Rev. Lett.*, **70**, 2174 (April 1993); 76, 2202 (1996).
[2] P. J. Haskins, et al., "Molecular Dynamics Studies of Fast Decomposition in Energetic Molecules," in *Eleventh Symposium (International) on Detonation* (1998), p. 897.
[3] W. Fickett and W.C. Davis, *Detonation* (University of California Press, Berkeley, 1979).
[4] B.M. Rice, et al., "Molecular-Dynamics Study of Detonation, ii. The Reaction Mechanism," *Phys. Rev. E*, **53**, 1 (January 1996) p. 623.

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